

WE CLAIM:

1. A metal-promoted aluminosilicate zeolite having improved stability formed by presteaming an aluminosilicate 5 zeolite at a temperature of 600°C. - 800°C. for a period of time of 0.25 to 8 hours, said presteaming not providing significant dealumination of said aluminosilicate zeolite, subsequently adding metal to said presteamed zeolite.

10 2. The stabilized aluminosilicate zeolite of claim 1, wherein said metal is iron.

15 3. The stabilized aluminosilicate zeolite of claim 1, wherein said metal is added in amounts of from 0.1 to 30% by weight calculated as metal based on the total weight of the metal and aluminosilicate zeolite.

20 4. The stabilized aluminosilicate zeolite of claim 3, wherein said metal is added in amounts of from 0.5 to 2.5 weight percent based on the total weight of the metal and the zeolite.

25 5. The stabilized aluminosilicate zeolite of claim 4, wherein said metal is iron which is present in amounts of 0.7 to 1.5 weight percent as iron based on the total weight of iron and the zeolite.

30 6. The stabilized aluminosilicate zeolite of claim 1, wherein said zeolite has a silica to alumina ratio of at least about 8, and a pore structure which is interconnected

in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7  $\text{\AA}$ .

7. The stabilized aluminosilicate zeolite of claim 6  
5 comprising zeolite beta.

8. A stable, metal-promoted aluminosilicate zeolite prepared by contacting an aluminosilicate zeolite with a lanthanide salt by ion-exchange and subsequent to contact  
10 with said lanthanide salt, adding a metal promoter by ion-exchange to said lanthanide-treated aluminosilicate zeolite.

9. The stabilized aluminosilicate zeolite of claim 8,  
wherein said lanthanide salt is a cerium salt.

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10. The stabilized aluminosilicate zeolite of claim 8,  
wherein said metal promoter is iron.

11. The stabilized aluminosilicate zeolite of claim 8,  
20 wherein said metal promoter is added in amounts of from 0.1 to 30% by weight calculated as metal based on the total weight of the metal and zeolite.

12. The aluminosilicate zeolite of claim 10, wherein  
25 said iron is added in amounts of from about 0.5 to 2.5 weight percent.

13. The stabilized aluminosilicate zeolite of claim  
12, wherein said zeolite is zeolite beta.

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14. The stabilized aluminosilicate zeolite of claim 8, wherein said zeolite has a silica to alumina ratio of at least about 8, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an 5 average kinetic pore diameter of at least about 7  $\text{\AA}$ .

15. The stabilized aluminosilicate zeolite of claim 14, wherein said metal promoter is iron which is added in amounts of from 0.5 to 2.5 weight percent as metal based on 10 the total weight of the metal and the zeolite.

16. A stabilized aluminosilicate zeolite containing alternating aluminum and oxygen atoms separate from the framework of said zeolite, said non-framework alternating 15 aluminum and oxygen atoms comprising at least 10 wt.% of total aluminum oxide in said zeolite.

17. The stabilized aluminosilicate zeolite of claim 16, comprising said non-framework alternating aluminum and 20 oxygen atoms in the form of a plurality of chains.

18. The stabilized aluminosilicate zeolite of claim 16, wherein said zeolite includes a metal promoter.

25 19. The stabilized aluminosilicate zeolite of claim 18, wherein said metal promoter is ion-exchanged into said zeolite.

20. The stabilized aluminosilicate zeolite of claim 30 19, wherein said metal promoter is iron and said zeolite is zeolite beta.

21. The stabilized aluminosilicate zeolite of claim 20, wherein said iron is present in amounts of 0.1 to 30 weight percent by weight calculated as metal and based on 5 the total weight of the metal and the zeolite.

22. The stabilized aluminosilicate zeolite of claim 21, wherein said iron is present in amounts of 0.5 to 2.5 weight percent based on metal.

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23. The stabilized aluminosilicate zeolite of claim 21, wherein said iron is present in the amounts of 0.7 to 1.5 weight percent based on iron.

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24. The stabilized aluminosilicate zeolite of claim 16, wherein said zeolite has a silica to alumina ratio of at least about 8, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic diameter of at least about 7  $\text{\AA}$ .

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25. The stabilized aluminosilicate zeolite of claim 24, further including a metal promoter.

26. A stabilized metal-promoted aluminosilicate 25 zeolite having an FT-IR absorption peak at  $3781\pm2 \text{ cm}^{-1}$ .

27. The stabilized aluminosilicate zeolite of claim 26, wherein said zeolite has a silica to alumina ratio of at least about 8, and a pore structure which is interconnected 30 in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7  $\text{\AA}$ .

28. The stabilized aluminosilicate zeolite of claim 27, wherein said zeolite is selected from the group consisting of ultrastable Y, beta and ZSM-20.

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29. The stabilized aluminosilicate zeolite of claim 26 selected from the group consisting of ZSM-5, ZSM-8, ZSM-11, ZSM-12, zeolite X, zeolite Y, beta, mordenite and erionite.

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30. The stabilized aluminosilicate zeolite of claim 26, wherein said zeolite is zeolite beta.

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31. The stabilized aluminosilicate zeolite of claim 26, wherein said metal promoter is present in amounts of 0.1 to 30 percent by weight calculated as metal and based on the total weight of the metal and the zeolite.

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32. The stabilized aluminosilicate zeolite of claim 26, wherein said zeolite is zeolite beta and said metal promoter is iron.

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33. The stabilized aluminosilicate zeolite of claim 32, wherein said iron is present in amounts of from 0.5 to 2.5 weight percent.

34. The stabilized aluminosilicate zeolite of claim 33, wherein said iron is present in amounts of from 0.7 to 1.5 weight percent.

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35. A stabilized aluminosilicate zeolite catalyst characterized by FT-IR absorption peak at  $3781\pm2\text{ cm}^{-1}$  and

wherein said peak has an area of at least 0.05 absorbance unit x  $\text{cm}^{-1}$ .

36. The stabilized aluminosilicate zeolite of claim 5 35, wherein said zeolite has a silica to alumina mole ratio of at least about 8, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7  $\text{\AA}$ .

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37. The stabilized aluminosilicate zeolite of claim 36, wherein said zeolite is selected from the group consisting of ultrastable Y, beta and ZSM-20.

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38. The stabilized aluminosilicate zeolite of claim 36, wherein said zeolite is zeolite beta.

39. The stabilized aluminosilicate zeolite of claim 35, which is ion-exchanged with a metal.

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40. The stabilized aluminosilicate zeolite of claim 39, wherein said metal comprises 0.1 to 30 weight percent by weight calculated as the metal and based on the total weight of the metal and the zeolite.

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41. The stabilized aluminosilicate zeolite of claim 40, wherein said zeolite is beta and said metal is iron.

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42. A process for improving the stability of an aluminosilicate zeolite catalyst under oxidizing and/or hydrothermal conditions, comprising treating said

aluminosilicate zeolite with steam at a temperature of 600°C. to 800°C. for a period of time of 0.25 to 8 hours without substantially dealuminizing said zeolite.

5       43. The process of claim 42, wherein the temperature of said steam is 650°C. to 750°C. and the length of treatment is from 0.5 to 4 hours.

10      44. The process of claim 43, wherein the length of the steam treatment is from 1 to 2 hours.

15      45. The process of claim 42, wherein said zeolite has a silica to alumina mole ratio of at least about 8, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7 Å.

20      46. The process of claim 45, wherein said zeolite is selected from the group consisting of ultrastable Y, beta and ZSM-20.

47. The process of claim 46, wherein said zeolite is zeolite beta.

25      48. The process of claim 42, wherein said zeolite is selected from the group consisting of ZSM-5, ZSM-8, ZSM-11, ZSM-12, X, Y, beta, mordenite, and erionite.

30      49. The process of claim 42 comprising adding a metal promoter to said steam-treated zeolite.

50. The process of claim 49, wherein said metal promoter is present in the amounts of 0.1 to 30 percent by weight calculated as metal and based on a total weight of the metal and the zeolite.

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51. The process of claim 50, wherein said zeolite is zeolite beta and said metal promoter is iron.

10 52. The process of claim 49, wherein said metal promoter is added by ion-exchanging said steam-treated zeolite with a metal salt.

15 53. A process for stabilizing an aluminosilicate zeolite catalyst for use under oxidizing and/or hydrothermal conditions comprising ion exchanging said aluminosilicate zeolite with a lanthanide salt under acidic conditions insufficient to substantially dealuminate said zeolite and to provide a level of lanthanide of approximately 0.25 to 1 weight percent based on lanthanide on said zeolite.

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54. The process of claim 53, wherein said lanthanide salt is a cerium salt.

25 55. The process of claim 53, wherein said zeolite has a silica to alumina mole ratio of at least about 8, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7  $\text{\AA}$ .

56. The process of claim 55, wherein said zeolite is selected from the group consisting of ultrastable Y, beta and ZSM-20.

5 57. The process of claim 53, wherein said zeolite is selected from the group consisting of ZSM-5, ZSM-8, ZSM-11, ZSM-12, X, Y, beta, mordenite and erionite.

10 58. The process of claim 53, wherein subsequent to ion exchange with said lanthanide salt, said treated zeolite is ion exchanged with a catalytic metal salt to add said catalytic metal to said zeolite by ion-exchange.

15 59. The process of claim 58, wherein said catalytic metal salt is an iron salt.

20 60. The process of claim 59, wherein said zeolite is zeolite beta and said iron is added to said zeolite in amounts from 0.1 to 30 percent by weight calculated as iron.

61. The process of claim 60, wherein said lanthanide salt is a cerium salt.

25 62. The process of claim 61, wherein the iron is present in amounts of 0.5 to 2.5 weight percent as metal on said zeolite.

30 63. The process of claim 62, wherein said iron is present in amounts of from about 0.7 to 1.5 weight percent as iron on said zeolite.

64. A method for the reduction of nitrogen oxides with ammonia, which comprises:

contacting a gaseous stream containing nitrogen oxides and ammonia at a temperature of from about 250°C. to 5 600°C. with a catalyst composition comprising: a metal-promoted aluminosilicate zeolite having improved stability formed by presteaming an aluminosilicate zeolite at a 10 temperature of 600°C. - 800°C. for a period of time of 0.25 to 8 hours, said presteaming not providing significant dealumination of said aluminosilicate zeolite, adding metal 15 to said presteamed zeolite, said zeolite having a silica to alumina mole ratio of at least about 8, and a pore structure which is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7 Å.

65. The method of claim 64, wherein said metal is added in amounts of from 0.1 to 30% by weight calculated as 20 metal based on the total weight of the metal and aluminosilicate zeolite.

66. The method of claim 65, wherein the metal promoter is present in the amount of from about 0.5 to 2.5 percent by weight of the total weight of the catalytic material.

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67. The method of claim 66, wherein the promoter comprises iron.

68. The method of claim 64, wherein the zeolite is 30 selected from the group consisting of USY, beta and ZSM-20.

69. The method of claim 67, wherein the zeolite is beta.

70. The method of claim 64, wherein the catalyst 5 composition further includes a refractory binder admixed with the zeolite.

71. A method for the reduction of nitrogen oxides with ammonia, which comprises:

10 contacting a gaseous stream containing nitrogen oxides and ammonia at a temperature of from about 250°C. to 600°C. with a catalyst composition comprising: a stable, metal-promoted aluminosilicate zeolite prepared by ion exchanging an aluminosilicate zeolite with a lanthanide salt 15 and subsequent to said ion exchange with said lanthanide salt, adding a metal promoter by ion-exchange to said lanthanide ion exchanged aluminosilicate zeolite, said zeolite having a silica to alumina mole ratio of at least about 8, and a pore structure which is interconnected in all 20 three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7  $\text{\AA}$ .

72. The method of claim 71, wherein said metal is added in amounts of from 0.1 to 30% by weight calculated as 25 metal based on the total weight of the metal and aluminosilicate zeolite.

73. The method of claim 72, wherein the metal promoter is present in the amount of from about 0.5 to 2.5 percent by 30 weight of the total weight of the catalytic material.

74. The method of claim 73, wherein the promoter comprises iron.

75. The method of claim 71, wherein the zeolite is  
5 selected from the group consisting of USY, beta and ZSM-20.

76. The method of claim 75, wherein the zeolite is  
beta.

10 77. The method of claim 71, wherein the catalyst composition further includes a refractory binder admixed with the zeolite.

15 78. A method for the reduction of nitrogen oxides with ammonia, which comprises:

contacting a gaseous stream containing nitrogen oxides and ammonia at a temperature of from about 250°C. to 600°C. with a catalyst composition comprising: (a) a stabilized aluminosilicate zeolite comprising non-framework chains of alternating aluminum and oxygen atoms separate from the framework of the zeolite, at least 10% of the aluminum oxide of said zeolite, being in the form of said non-framework chain, said zeolite having a silica to alumina mole ratio of at least about 8, and a pore structure which 25 is interconnected in all three crystallographic dimensions by pores having an average kinetic pore diameter of at least about 7 Å.; and (b) a metal promoter.

79. The method of claim 78, wherein said metal is  
30 added in amounts of from 0.1 to 30% by weight calculated as

metal based on the total weight of the metal and aluminosilicate zeolite.

80. The method of claim 79, wherein the metal promoter  
5 is present in the amount of from about 0.5 to 2.5 percent by weight of the total weight of the catalytic material.

81. The method of claim 80, wherein the promoter comprises iron.

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82. The method of claim 78, wherein the zeolite is selected from the group consisting of USY, beta and ZSM-20.

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83. The method of claim 82, wherein the zeolite is beta.

84. The method of claim 78, wherein the catalyst composition further includes a refractory binder admixed with the zeolite.

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85. A method for the reduction of nitrogen oxides with ammonia, which comprises:

contacting a gaseous stream containing nitrogen oxides and ammonia at a temperature of from about 250°C. to 25 600°C. with a catalyst composition comprising: a stabilized metal-promoted aluminosilicate zeolite having an FT-IR adsorption peak at  $3781\pm2\text{ cm}^{-1}$ .

86. The method of claim 85, wherein said metal is added in amounts of from 0.1 to 30% by weight calculated as metal based on the total weight of the metal and aluminosilicate zeolite.

87. The method of claim 86, wherein the metal promoter is present in the amount of from about 0.5 to 2.5 percent by weight of the total weight of the catalytic material.

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88. The method of claim 87, wherein the promoter comprises iron.

89. The method of claim 85, wherein the zeolite is  
10 selected from the group consisting of USY, beta and ZSM-20.

90. The method of claim 89, wherein the zeolite is  
beta.

15 91. The method of claim 85, wherein the catalyst composition further includes a refractory binder admixed with the zeolite.

92. The method of claim 64, wherein said gaseous  
20 stream is contacted with said catalyst at a temperature of greater than 500°C.

93. The method of claim 71, wherein said gaseous stream is contacted with said catalyst at a temperature of  
25 greater than 500°C.

94. The method of claim 78, wherein said gaseous stream is contacted with said catalyst at a temperature of greater than 500°C.

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95. The method of claim 85, wherein said gaseous stream is contacted with said catalyst at a temperature of greater than 500°C.

5 96. The stabilized aluminosilicate zeolite catalyst of claim 35, wherein said peak has an area of at least 0.1 absorbance unit  $\times$   $\text{cm}^{-1}$ .

10 97. The stabilized aluminosilicate zeolite catalyst of claim 35, wherein said peak has an area of at least 0.2 absorbance unit  $\times$   $\text{cm}^{-1}$ .

98. The method of claim 85, wherein said peak as an area of at least 0.05 absorbance unit  $\times$   $\text{cm}^{-1}$ .

15 99. The method of claim 85, wherein said peak as an area of at least 0.1 absorbance unit  $\times$   $\text{cm}^{-1}$ .

20 100. The method of claim 85, wherein said peak as an area of at least 0.2 absorbance unit  $\times$   $\text{cm}^{-1}$ .